

SOLVENT DEPENDENT PHOTOISOMERIZATION OF POLYENE NITRILES¹

by

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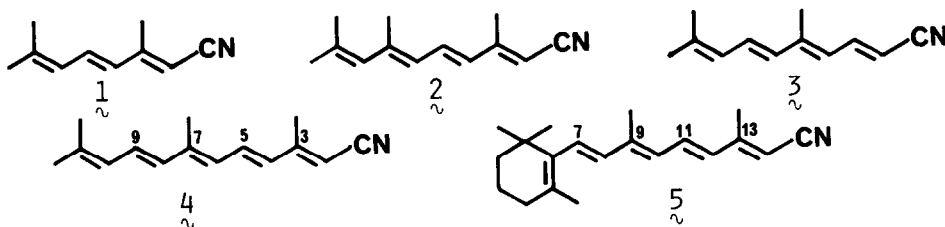
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The initial product ratios of several polyene nitriles, which do not have low lying n, π^* states, are reported. The solvent dependent chemistry has been discussed in conjunction with the well known retinal chemistry.

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Combining the results of photoisomerization of the polyenals and polyenones in the retinal series² and photophysical data obtained by Das and Becker,³ Ramamurthy et al. suggested that the well known solvent dependent photoisomerization of retinal⁴ was due to switching of the role of the reactive states: n, π^* state in non-polar solvents and π, π^* state in polar solvents.² The solvent dependent photoisomerization of polyene esters^{5,6} could conceivably be due to the same effect although the exact position of their n, π^* states are not well defined. We now wish to report results of photoisomerization of polyene nitriles, which because of the symmetry of the cyano group do not have a low lying n, π^* state.⁷

The following compounds have been prepared for the current study starting from 3-methyl-2-butenal (the " C_5 -aldehyde"), mesityl oxide or β -ionylideneacetaldehyde (the " C_{15} -aldehyde") by conventional modified Wittig reactions:⁸



In all cases the trans isomer was the main isomer in the synthetic mixture, together with smaller amounts of the cis isomers around the trisubstituted double bonds. Those hindered isomers not present in synthetic mixtures (e.g. 4-cis in 1, 2 and 4, and 11-cis in 5) were isolated by preparative hplc from the corresponding photostationary mixtures.⁹ All isomers were characterized by their ¹H-nmr spectra (80MHz or 300MHz).¹⁰

Only results obtained from direct irradiation of the all-trans isomers of these compounds are presented. Typically the experiment involved irradiation of a deoxygenated dilute solution (approx. .01M) of a polyene nitrile in either a non-polar (hexane or cyclohexane) or a polar solvent (acetonitrile). The reaction was followed by hplc analyses. Initial product ratios were determined during early stages of reactions (less than 10% conversion) and after

correcting the difference in absorptivity of isomers at the wavelength of analysis. Results are summarized in the last two columns of Table 1.¹¹

The pattern of product variation of the two pentaene nitriles (4 and 5) in different solvents is reminiscent of the results of retinal, related analogues^{12,13} and esters:^{5,6} i.e., the hindered isomer (11-cis in retinal and retinonitrile and 4-cis in 4) is formed only in polar solvents. This pattern is consistent with the view that in a non-polar solvent the reaction proceeds in a selective manner favoring isomerization at the more crowded trisubstituted double bonds and less selective in a polar solvent isomerizing at disubstituted as well as trisubstituted double bonds. Same as the shorter chain carbonyl compounds the lower member polyene nitriles, are less sensitive to solvent polarity. The planar tetraene nitrile 2 nevertheless shows a more pentaene like photochemical property in that the disubstituted 4-cis isomer, while present in cyclohexane, increased more than tenfold in acetonitrile. This is somewhat different from the tetraenone (the "C₁₈-ketone") in the vitamin A series but consistent with the different extent of planarity of the two compounds.

Considering the absence of low-lying n, π^* states in the nitriles, the similarity of the photochemical properties between the two series of compounds appears surprising. But upon reflection the existence of an explanation not involving the n, π^* state to account for the solvent dependent photochemistry becomes evident.

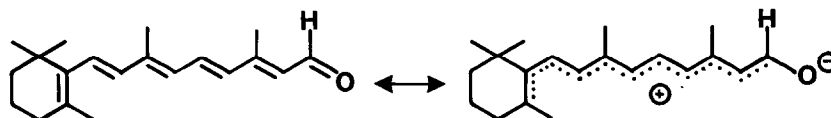
The zwitterionic character of the orthogonal π, π^* excited states of polyenes,¹⁴ is probably not a contributing cause for the solvent effect because charge separation becomes dominant only at a geometry near the perpendicular structure (the "sudden polarization effect").¹⁵ Any solvent interaction with this zwitterionic species is clearly too late to have an effect on product distribution. On the other hand for a negatively substituted polyene, the planar excited species (π, π^*) appear to have a high dipolar character. For example for retinal, both

Initial Product Ratio from Direct Irradiation of all-trans Polyene Nitriles^a

Cpd	Solvent	Detecting beam, nm	% Conversion	4-cis/2-cis ^b	6-cis/2-cis ^b
1	Cyclohexane	280	3.74	.07	--
	CH ₃ CN		5.97	.14	--
2	Cyclohexane	340	5.79	.03	.20
	CH ₃ CN		5.88	.39	.18
3	Cyclohexane	340	8.10	8.8	--
	CH ₃ CN		7.43	3.1	--
4	Cyclohexane	390	3.95	0	.25
	CH ₃ CN		5.65	1.04	.74
5	n-Hexane	350	1.94	0 ^c	.78 ^d
	CH ₃ CN		5.07	1.87	1.78

a. Hanovia medium pressure 200W Hg lamp with appropriate filter plates: 1, Pyrex (>280nm); 2 and 3, Corning 0-52 (>350nm); 4, Corning 0-51 (>380nm); 5, Corning 0-52 and 7-60 (360nm). b. After correction of differences in response of isomers to the detecting beam. c. 11-cis/13-cis. d. 9-cis/13-cis.

experimentally¹⁶ and computationally¹⁷ it has been shown that its dipole moment increases significantly (by threefold) during electronic excitation. In other words the dipolar resonance structure is a major contributing structure in the excited state while only a minor one in the ground state. Associated with a charge redistribution is a further decrease of the excited state bond order of the double bonds during the excitation process, thus facilitating the isomerization process.



The extent of charge redistribution is a function of polarizability of the molecule which in turn depends on the length of conjugation (ionization potential) and the dielectric constant of the medium. Hence in shorter chain compounds their excited structures are not sufficiently polarized to interact strongly with solvent for a significant solvent dependent photochemical behavior. On the other hand for a longer polyene, such as a pentaene in a non-polar solvent, while the decreased excited state bond order is sufficient to bring about selective isomerization at the trisubstituted double bonds, only when the π -bond order is further decreased by the enhanced dipolar character through interaction with the polar solvent then isomerization becomes a random process taking place at both the disubstituted and the trisubstituted double bonds.

There are two possibilities for the reactive π, π^* state.¹⁸ The " $^1B_u^+$ " state is clearly the initially populated state; spectroscopic studies on the other hand indicate that the lowest excited state is of " $^1A_g^-$ " symmetry.¹⁷ Interestingly calculations seem to show that both the "ionic $^1B_u^+$ " and the "covalent $^1A_g^-$ " states¹⁸ are highly polarized with dipole moments substantially larger than that of the ground state.¹⁷ A plausible pathway of deactivation is internal conversion from " $^1B_u^+$ " to the " $^1A_g^-$ " state where fluorescence competes against chemistry (twisting of the formal double bonds). Solvent polarity only causes a redistribution of the π -electrons and re-ordering of the excited bond orders. It should be mentioned that this conclusion is consistent with the recent calculated results that solvent polarity is insufficient to cause reversal of ordering of the two π, π^* states¹⁷ which ruled out the latter being a possible explanation for the solvent dependent photochemistry.¹⁹

It is interesting to speculate how the current interpretation affects the earlier explanation for the enones and enals. There is no doubt that the n, π^* state dominates the photochemical and spectroscopic properties of the shorter chain carbonyl compounds. The unusually long fluorescence lifetime of retinal in polar solvents^{3,17} is consistent with a low-lying " $^1A_g^-$ " state, thus in agreement with both the current and the earlier interpretation of reversal of the n, π^* and π, π^* states.² However, in a non-polar solvent retinal being non-fluorescent the situation is less clear. The similar photochemical properties between retinal and retinonitrile under such conditions are suggestive of identical excited states for the two compounds (hence π, π^* for both cases). However, the possibility of an n, π^* state with photochemical properties very similar to a less polarized π, π^* state has not been ruled out.²⁰

References and Footnotes

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9. For example, the order of elution of isomers of 4 on an Ultrasphere Si-60, 5 μ , 10 x 250mm column with 0.65% ether/hexanes is: 4-cis, 6-cis, 2-cis,6-cis, 2-cis and all-trans.
10. ¹H-nmr data for isomers of 5 are listed in ref. 8. Data for 1 to 4 will be discussed in detail in a future full paper.
11. Photostationary state compositions have also been determined for all compounds. They show similar pattern of solvent dependence although the mixtures are more complex due to the presence of dicis isomers.
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19. Rigorously we have not ruled out another possibility where the photochemistry originates from the upper "¹B_u⁺" state and emission from the lower "¹A_g⁻" state. The relatively high quantum yields of isomerization make it less likely a S₂ process. Calculations also suggest that reaction from S₂ is an unlikely process (unpublished results, kindly provided by Professor R. R. Birge via private communication).
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